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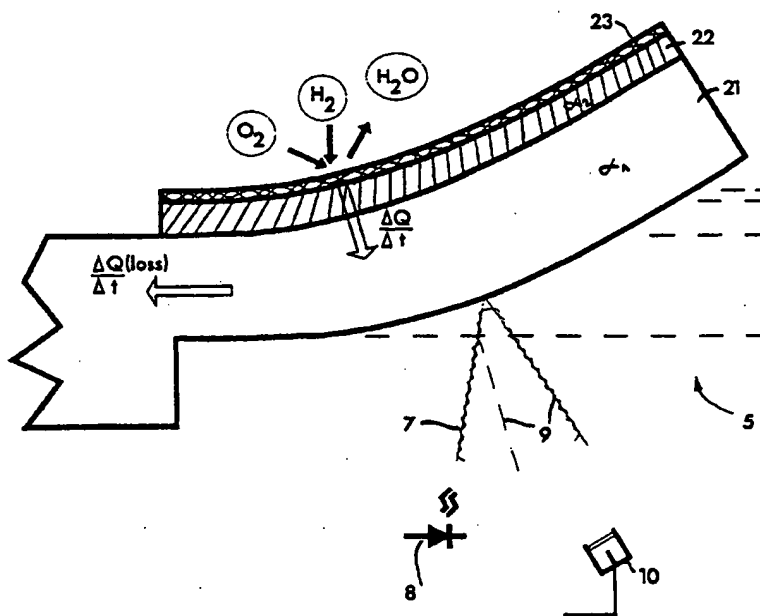
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**(54) Title:** CALORIMETRIC SENSOR**(57) Abstract**

A calorimetric sensor is described, in which a bimetallic lever (21, 22) is combined with a chemical sensing layer (23), e.g. a catalyst, and a sensitive device (6) to determine any deflection of the bimetallic lever. Due to its high sensitivity, the new sensor is applicable in various technical fields.



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## DESCRIPTION

### Calorimetric Sensor

5

The invention relates to a calorimetric sensor. Specifically, it pertains to a calorimetric gas sensor. A calorimetric gas sensor measures gas concentrations as a function of the temperature change produced by the heat of an reaction on its surface covered by a chemical sensing layer, in particular by a catalyst.

### BACKGROUND OF THE INVENTION

15 The technical field of the invention are calorimetric sensors. The known calorimetric sensors are produced by combining a sensitive calorimeter, a catalytic surface, and, if necessary, a heater to maintain the catalyst at a desired operating temperature.

Most commonly, the calorimeter is a thermo-electric transducer converting the thermal signal into an electrical signal. It is commonly known to use a thermocouple or a resistance thermometer as such a transducer. The simplest known form of a catalytic gas sensor is a simple platinum coil. The platinum coil is able to act, both, as a heater and as a temperature sensor. Platinum also serves as an active catalyst for reactions like the hydrocarbon oxidation.

Also the platinum coil sensor might still be used in spot reading instruments, it is not well suited for use in continuous operation due to a degradation of the catalyst. Improvement have been made by using more active catalysts, such as porous platinum, porous rhodium, or palladium (oxide) finely dispersed in thorium dioxide (thoria), and the like. Microcalorimeters based on these materials are also known as pellistors. A detailed description of catalytic gas sensors can be found, for example, in GB-A-1501888. However,

1 the known calorimetric gas sensor is used mostly as a quantitative device for  
the measurement of gases at high concentrations, e.g. as to detect an  
explosive gas mixture. The sensitivity of the known devices is limited to the  
range above 100 ppm. This is not enough to exploit these devices in fields  
5 which require a sensitivity for traces of a gas, as, for example, in toxicologic  
applications.

A higher sensitivity is achieved by a class of gas sensors known as  
metal-oxide gas sensors. Metal-oxide gas sensors are based on the electrical  
conductivity changes induced in a layer of metal oxide by gas adsorption on  
10 its surface. Mostly, inorganic materials such as oxides of tin and zinc are  
employed as sensing layers. Metal-oxide gas sensors are applied, for  
example, for monitoring the exhaust gases from internal combustion engines  
with a view to control the air/fuel ratio. As inorganic materials usually have to  
be operated at elevated temperatures, considerable efforts are known to  
15 exploit the properties of organic materials. These efforts are concentrated on  
phthalocyanine and porphyrin based materials containing different metal ions.  
It is an object of the invention to introduce a new calorimetric sensor. In  
particular, it is an object of the invention to enhance the sensitivity of the  
known sensors based on calorimetric principles. A further object of the  
20 invention is to develop a calorimetric gas sensor suitable for the trace  
analysis of gas mixtures. Yet another object of the invention is to supply a  
miniaturized calorimetric gas sensor designed for an integrated circuitry,  
especially in the form of arrays of such sensors.

25

#### SUMMARY OF THE INVENTION

The new catalytic gas sensor comprises a flexible element with a least two  
layers of material having a different thermal expansion coefficient and one of  
30 said layers or another layer able to act as chemical sensing layer, and means  
to detect the deflection of said flexible element.

1 The new sensor is based on what is commonly known as bimetal or  
thermobimetal effect. Bimetal switches have found a wide spread application  
in many devices, though being more and more replaced by electronic devices.  
In principle, a bimetallic temperature sensor is made of two tightly bonded  
5 layers of materials differing in their respective thermal expansion coefficient.  
These materials do not necessarily have to be metals. Therefore, the term  
"bimorph" is used as a less known but more precise synonym for "bimetallic".  
In case of a temperature change, both material elongate by different amounts,  
thus, introducing a bending or deflection of the flexible element from its  
10 original shape or position. In a first approximation, the bending radius of a  
thin bimorph strip is given by  $R = l/(\alpha_1 - \alpha_2)\Delta T$  with  $l$  being the length of the  
strip,  $\alpha_1, \alpha_2$  being the respective thermal expansion coefficients of the two  
bonded materials, and  $\Delta T$  being the temperature difference. The known  
bimetallic devices, however, have sizes within the centimeter range, making  
15 them unacceptable for any use besides a crude temperature measurement.  
No bimetallic device is known which is combined with a chemical sensing  
layer and able to detect a chemical reaction involving said layer.  
Though the invention makes use of the bimetallic effect, the dimensions of the  
new device are reduced to below one millimeter, reducing simultaneously the  
20 thermal capacity and the heat flow out of the device and, thus, enhancing the  
sensitivity of the device.  
As for the materials, themselves, there are, in principle, no constraints upon  
the shape of the flexible element used in the new device. However, to  
enhance sensitivity, it has preferably a beamlike shape or is formed like a  
25 triangle with a punched central portion, in which the length surmounts the  
width by approximately a factor of 10. Calculations based on the simple case  
of a beam as flexible element show that an optimum sensitivity can be  
achieved by using long thin beams. However, thermally induced noise makes  
it desirable to utilize a flexible element with a spring constant of above  $1 \text{ N}$   
30  $\text{m}^{-1}$  and a high resonance frequency. These conditions, together with a  
demand for a fast response time, enable a skilled person to optimize the new  
sensor in accordance with any imposed requirement.

1 A further enhancement of the sensitivity of the flexible element can be  
achieved by using more refined designs, e.g. by separating the two layers  
with different expansion coefficients leaving only at a few points bridges as a  
connection. However, these flexible elements have to be prepared with higher  
5 accuracy than the simple elements described above. As the silicon  
technology is the most developed technology for producing miniaturized  
devices, it is of advantage to use materials based on silicon for the  
preparation of the bimorph flexible elements. For example, Petersen  
describes in the IEEE Transactions on Electron Devices, Vol.ED-25, No.10,  
10 October 1978, pp. 1241-1250, the preparation of metal coated cantilevers on  
silicon wafers. From other sources, the preparation of beams of SiN by  
anisotropic chemical etching is known. Other feasible methods for preparing  
the desired flexible element are focussed beam techniques, reactive ion  
etching, and x-ray or synchrotron lithography in combination with galvano- or  
15 electroforming.

The second layer has advantageously a thermal expansion coefficient  $\alpha_2$   
which differs substantially from the thermal expansion coefficient  $\alpha_1$  of the  
main material of the flexible element. Suitable materials are, for example,  
metals like Al and Au, which are easily applicable onto the surface of Si and  
20 SiN.

To make the bimorph or "bimetallic" element a tool for monitoring even small  
amounts of gases, the means to detect the deflection of this element has to be  
very sensitive. Several accurate methods to detect the bending of a cantilever  
are known from the field of atomic force microscopy (AFM). The AFM is  
25 known as a device to examine the roughness of a surface. For that purpose, a  
cantilever is applied with a microscopic tip and scanned across the surface to  
be examined. It is found that the methods applied in AFM to detect the  
deflection of the cantilever can be advantageously employed in the new  
device. With the help of these methods, lever deflections of the order of less  
30 than 1 nm can be easily detected. In addition, motions of the lever ranging  
from 0.001 nm up to 100  $\mu\text{m}$  can be monitored, giving the new sensor a  
possible dynamic range of  $10^9$ . It is well within the scope of an averaged

1 skilled person to choose one of the available methods known in the field of  
atomic force microscopy as means to detect the deflection of the flexible  
element.

One group of these detecting methods is based on coupling the cantilever to  
5 another distance sensitive microscope. A combination of the cantilever with a  
scanning tunneling microscope is described, for example, in the patent  
US-A-4724318. Another approach using an evanescent wave coupling sensor,  
also known as scanning near-field optical microscope (SNOM) or scanning  
tunneling optical microscope (STOM), is described by Diaspro and Aguilar in:  
10 Ultramicroscopy 42-44 (1992), pp. 1668-1670.

Another group of detecting methods is based on the well known piezoelectric  
or piezoresistive effect. An example is described in: M. Tortonese et al., Appl.  
Phys. Lett. 62(8), 1993, pp.834-836. These methods provide detection  
schemes in which the deflection detector is integrated in the cantilever.

15 Yet another feasible way of detecting the displacement of the cantilever relies  
on capacitance sensing and is known, for example, from Joyce et al., Rev. Sci.  
Instr. 62(1991), p. 710, and Göddenhenrich et al., J. Vac. Sci. Technol.  
A8(1990), p. 383.

It is also possible to use the changes in the resonance frequencies of the  
20 flexible element to measure its bending. The fundamentals of this technique  
are known and described for example in the patent US-A-3413573.

The displacement of the flexible element can also be measured by applying  
optical methods, such as beam deflection or interferometry. The beam  
deflection method makes use of the length of the lever. Usually, a light beam,  
25 preferably produced by a laser diode or guided through an optical fiber, is  
directed onto the lever. A small deflection of the lever causes a reasonable  
change in the reflecting angle and, therefore, results in a deflection of the  
reflected light beam that is measured with bicell or other suitable photo  
detectors. The beam deflection method is simple and reliable. Interferometric  
30 methods are described, for example, by Martin et al., J. Appl. Phys. 61(1987),  
p.4723, by Sarid et al., Opt.Lett. 12(1988), p.1057, and by Oshio et al.,  
Ultramicroscopy 42-44(1992), pp.310-314.



1     Though it is possible to use one of the two "bimetallic" layers simultaneously  
as a chemical sensing layer, in most cases a third, distinct layer acting as a  
sensing element is required. This chemical sensing layer does not  
necessarily has to be a catalyst, even though a catalyst as chemical sensing  
5     layer forms a preferred embodiment of the invention. However, the high  
sensitivity of the new sensor makes it possible to exploit even the heat  
transfer occurring during ad- or absorption of molecules at the surface of the  
sensing layer. Therefore, a layer can be chosen which enables a selective  
ad- or absorption of the molecules to be detected. Thus, the term "chemical  
10    sensing layer" is used to specify the broader scope of the new sensor.

An ideal catalyst is defined as a substance that increases the rate at which a  
chemical reaction approaches equilibrium, without itself becoming  
permanently affected by the reaction. The catalyst achieves this enhancement  
by providing an alternative reaction path, involving different activated  
15    complexes, with a lower activation energy than the uncatalysed reaction  
mechanism. A wide range of catalysts for many different chemical reactions is  
known. For measurements using the catalytic oxidation of hydrogen,  
carbonmonoxide, hydrocarbons and other combustible gases, for example, the  
transition metals Pt, Pd, Rh, Ir, or their oxides, or a mixture of those materials  
20    are preferably applied. It is possible to provide a surface of the cantilever  
with a thin catalyst layer by using known deposition techniques, such as  
sputtering, epitaxial methods or electrochemical deposition. The surface of a  
deposited film can be further enlarged or roughened by etching with a  
suitable chemical agent.

25    As said above, another embodiment of the chemical sensing layer is a  
material which enables a chemisorption, i.e. the formation of chemical bonds  
between the (surface) molecules of said layer and those molecular species to  
be detected. The enthalpy of a chemisorptive process is known to range from  
approximately 40 kJ/mol to 400 kJ/mol. An energy transfer in this amount can  
30    readily be detected by the new sensor. Suitable materials are, for example,  
Ni, Fe, Ag, and Pt. The sensitivity of the new device allows in principle also  
the detection of adsorption, the energy of which is ranging from 0.3 kJ/mol to

1     3 kJ/mol, i.e. less than a tenth of the energy found at catalytic reactions or chemisorption.

By being able to detect chemisorption and adsorption, the new sensor also forms a valuable device to monitor biochemical processes: The chemical  
5     sensing layer in this case is advantageously a Langmuir-Blodgett (LB) film applied to the bimorph cantilever by known methods. Using the defined hydrophilic or hydrophobic surface of the LB film and the affinity between certain molecules, such as proteins and enzymes, it is, thus, possible to tailor a highly specific sensor suitable not only for gas analysis but also for medical  
10    test methods, e.g. immunoassay systems. The vast state of art concerning LB films is, for example, referred to in: G.G. Roberts (ed.), Langmuir-Blodgett Films, Plenum, New York, 1990. A method for applying a LB film to the surface of a semiconducting surface is detailed by S. Lee et al., Sensors and Actuators B, 12 (1993), pp.153-154.

15    By changing the temperature, a chemisorption can be reversed, e.g. the chemisorption of hydrogen on nickel or platinum. Many catalytic reactions equally require an initial temperature. The difference in the initial temperature allows to inhibit and suppress undesired reactions. These temperature dependent reactions can be effectively exploited when using the sensor as an  
20    analyzing tool. In general, it is more convenient to provide the necessary temperature by heating the chemical sensing layer than by heating the reactants, themselves. As to this reason, the sensor preferably comprises a heating device for the chemical sensing layer. The sensing layer can be heated by a juxtaposed electrical heater, i.e. a thermoelement, or by using  
25    electromagnetic radiation.

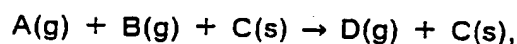
In a preferred embodiment of the invention, the chemical sensing layer is heated by the same light emitting device which is employed for measuring the deflection of the flexible element by using the above described beam deflection method.

30    The sensitivity of the new device is enhanced by employing a pair of flexible elements only one of which is covered by a chemical sensing layer. This embodiment of the invention has intrinsic reference or calibration properties,

1 as both levers bend by the same amount for temperature changes not related to a chemical reaction resulting in a zero difference signal. The desired reaction, however, only effects the bending of the covered lever and is, thus, detected with an enhanced accuracy.

5 By combining levers coated with different chemical sensing layers and/or levers held at different temperatures, it is possible to manufacture an artificial nose, able to identify and analyze different gas mixtures. Catalysts specifically sensitized to a single molecule for analyzing purposes readily simplifies the identification of a substance. However, in cases where no such catalyst is available, the levers can be held at different temperatures to obtain the reaction activation energy by evaluating the reaction rate, in particular, if a simple Arrhenius relationship holds between the reaction rate and the temperature. Interferences between several substances may be eliminated by applying multicomponents analysis techniques known per se.

15 In the following, the model (catalytic) reaction



is taken as an example to illustrate the operating principles of the sensor according to the invention. The reaction describes the formation of a gaseous substance D from the two gaseous reactants A and B accelerated by the solid catalyst C left unchanged.

20 Associated with the reaction is an enthalpy of formation  $\Delta H$ , giving the amount of heat released to (exothermic reaction) or absorbed from (endothermic reaction) the surrounding per mass unit. In the following, the reaction is assumed to be exothermic, i.e.  $\Delta H < 0$ . Thus, the formation rate, i.e. the reaction velocity, is corresponding to a certain amount of heat produced per time unit. Except for losses to the surrounding, the heat causes a temperature rise  $\Delta T$  in the cantilever coated with the catalyst until the formation of heat is balanced by the losses. The change in temperature causes the lever to bend, as it is made of materials with different thermal expansion coefficient. Thus, 25  $\Delta T$  corresponds to a deflection of the flexible element from its previous position, which is measured by the means described above. An equal

1 behaviour applies if the reaction is endothermic. In this case, the cooling  
induced by the reaction causes the bimorph lever to bend.  
By measuring the deflection as such, the sensor presents a highly sensitive  
detector for the appearance of a certain substance. By using an appropriate  
5 calibration to determine the relation between the reaction velocity and the  
amount of deflection, the sensor is useful for quantitative measurements, too.  
Due to its sensitivity and small dimensions the sensor can provide a valuable  
tool for controlling chemical processes. In particular, it can be use to detect  
toxic or combustive gases in air, especially to monitor the exhaust gases of  
10 combustion engines and other environmental hazards. Covered by an  
appropriate chemical sensing layer, the new sensor is also applicable in  
analysing biochemical reactions and as a tool for performing medical tests.

#### 15 DESCRIPTION OF THE DRAWINGS

The invention is described in detail below with reference to the following  
drawings:

20 **FIG. 1** schematically shows an embodiment of the new sensor and an  
apparatus for testing it.

**FIGs. 2A,B,C** show a component of the new sensor in different embodiments.

25 **FIG. 3** shows a plot of the deflection of a sensor according to the  
invention versus the power of laser radiation.

**Fig. 4** illustrates the behaviour of the flexible element under operating  
conditions.

30 **Fig. 4** shows an embodiment of the invention having intrinsic reference  
properties.

1     **Fig. 5**            shows an array of sensors as a one chip device.

## EXAMPLES

5

An embodiment of the new sensor according to the invention is tested by using a conventional atomic force microscope (AFM). FIG. 1 shows a vacuum chamber 1, an inlet 2 for test gas mixtures and an outlet 3 leading to the pumping system (not shown). The chamber 1, further, comprises a holder 4 to mount the flexible element, the cantilever 5 which serves as such flexible element, and a beam deflection system 6 for determining the deflection of the cantilever 5. A light beam 7 is generated by a laser diode 8. In operation, the beam 7 is reflected from the cantilever 5 and the reflected beam 9 is surveilled by a two sectors of a quadrant detector 10. The quadrant detector is operated in the  $(A-B)/(A+B)$  mode to normalize for fluctuations in the laser power. The beam deflection system comprises means 11 to determine the deflection of the cantilever 5 using the signals received the detector 10.

To demonstrate the operating principle of the new sensor as a calorimeter, a beam-shaped bimorph cantilever as shown in FIGs. 2A,B is employed. The cantilever's base material 21 is Silicon with a thickness of  $1.5 \mu\text{m}$  coated by a  $0.4 \mu\text{m}$  thick layer 22 of Al using a vacuum evaporation technique. Both layers 21, 22 have thermal expansion coefficients  $\alpha_1, \alpha_2$  which differ significantly as having the values  $3 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  for Si and  $25 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  for Al. The layers 21, 22, thus, form the desired bimorph or "bimetallic" junction. Using again vacuum evaporation, a 40 nm thick Pt layer 23 is deposited on top of the AL layer to act as catalyst. The overall dimensions of the applied cantilever are:  $l=400 \mu\text{m}$ ,  $w=35 \mu\text{m}$ , and  $t=1.94 \mu\text{m}$ .

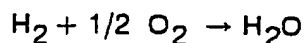
The linearity and the response time of the sensor are tested by varying the output power the laser diode 8 from  $400 \mu\text{W}$  to  $600 \mu\text{W}$ . As shown by FIG. 3, the deflection of the bimorph cantilever relates linear to the heat transfer induced by radiation of the laser diode the power of which ranges from  $400 \mu\text{W}$  to  $600 \mu\text{W}$ . The data further show that an effective heating of the

1 cantilever can be achieved by using the laser radiation of the deflection beam system. Thus, it is possible to heat the chemical sensing layer 23 above the ambient temperature.

By measuring the response of the cantilever 5 to a laser pulse of 300  $\mu$ W, a  
5 response time of approximately 1 ms is determined for a device according to the example.

In another example, the new sensor is applied to monitor a chemical reaction. A triangularly shaped cantilever 5 is used as illustrated by FIGs. 2A,C. The cantilever's base material 21 is silicon nitride (SiN), coated by a 0.2  $\mu$ m thick  
10 layer 22 of Al using vacuum evaporation. Using the same technique, again, a layer 23 of Pt is deposited onto the alumina as catalyst. The layer 23 has a thickness of 20 nm. As in the previous example, fine intermediate layers formed by the oxidation of the freshly etched or deposited surface are not taken into account as separate layers. The dimensions (see FIGs. 2A,C) of the  
15 cantilever are:  $l = 200 \mu\text{m}$ ,  $w = 20 \mu\text{m}$ , and  $t = 2 \mu\text{m}$  with a force constant of approximately  $0.1 \text{Nm}^{-1}$ .

Referring to FIGs. 1 and 4, the device is tested by using the reaction:



20 with a reaction enthalpy of 242 kJ/mol, catalyzed by the Pt layer 23. First, the vacuum chamber 1 is pumped to a pressure of  $10^{-5}$  mbar to remove unwanted gaseous residues. Then, the chamber is filled with a mixture of  $\text{H}_2$  and  $\text{O}_2$  in the correct stoichiometric ratio (2:1) up to a pressure of  $2 \times 10^{-2}$  mbar.

25 Due to the heat production  $\Delta Q/\Delta t$  of the reaction at the catalytic surface 23, the temperature of the cantilever 5 rises until the produced heat is balanced by the heat losses  $\Delta Q(\text{Loss})/\Delta t$ . The temperature rise corresponds to a bending of the cantilever as depicted in FIG. 4. After bending, the laser beam 9 is reflected in a slightly different angle compared to the unbended case.  
30 The difference is measured by the detector 10. Under the described conditions, the cantilever was deflected by 150 nm, thus, giving a theoretical

1 detection limit for hydrogen of  $10^{-7}$  mbar, as a deflection of 0.1 nm can still  
be detected under optimum conditions.

It is further possible to enhance the sensitivity of the sensor by eliminating  
some of the background noise by using a device which compensates for  
5 temperature shifts not caused by the catalytic reaction, itself. An example of  
such a device with an intrinsic calibration is shown in FIG. 5. It comprises a  
second lever 51 almost identical to the first lever 5 lacking, however, a  
chemical sensitive layer 23. The deflection of each lever is measured with the  
same means 6 as described above (see FIG. 1), additionally comprising means  
10 52 to determine the difference between the deflection of both lever 5, 51. By  
measuring the deflections of both levers and evaluating their difference, the  
background shifts due to changes in temperature and other effects are  
diminished.

By coupling several sensors (with intrinsic calibration), each sensitized to a  
15 different species A, B, C, D, E, F, and G, as illustrated by FIG. 6, a  
multi-component analyzer is realized. Letters A', B', ..., and G' denote the  
uncoated reference levers used to eliminate the background noise. Though a  
careful choice of the catalysts and temperature conditions has to be made by  
a skilled person, the fundamental principles of the device remains unchanged:  
20 An analysis of the deflection of each lever or pair of lever gives the amount of  
the component for which the lever has been sensitized. Interferences  
occurring due to a partial sensitivity of a catalyst for more than one species  
can be filtered out by an appropriate mathematical method.

As all components (levers, laser diodes, photo detectors, etc.) are producible  
25 on the semiconducting base material (Si), it is readily feasible to manufacture  
also large arrays of the sensor on a single-chip basis.

## 1 CLAIMS

1. A calorimetric sensor, especially a calorimetric gas sensor, comprising  
a flexible element (5) with at least two layers (21, 22) of materials with  
different thermal expansion coefficients, one of which is a chemical  
sensing layer (23), and means (6) for determining the deflection of said  
flexible element (5).
2. A sensor in accordance with claim 1, comprising  
at least two layers (21, 22) of materials with different thermal expansion  
coefficients and at least one chemical sensing layer (23).
3. A sensor in accordance with claim 1, wherein  
the means (6) for determining the deflection of the flexible element (5) is  
chosen from a group comprising means for measuring the tunnel current  
between the flexible element (5) and a probing tip, means for measuring  
the intensity of an evanescent electro-magnetic wave guided through the  
flexible element (5), means for determining a piezo-electric/resistive  
change of the flexible element (5) while bending, means for measuring the  
capacity between the flexible element (5) and another surface,  
interferometric means, and beam deflection means.
4. A sensor in accordance with claim 1, comprising  
means for heating the chemical sensing layer (23).
5. A sensor in accordance with claim 3, wherein  
the heating means is a resistance heater, or a thermoelement, or an  
emitter (8) of intensive electromagnetic radiation.
6. A sensor in accordance with claim 1, wherein  
the chemical sensing layer (23) is a catalytic layer.
7. A sensor in accordance with claim 1, wherein  
the chemical sensing layer (23) is a catalytic layer comprising a transition  
metal, or an oxide of said metal, or a combination of those materials.
8. A sensor in accordance with claim 1, wherein  
the chemical sensing layer (23) comprises an organic material, preferably  
a Langmuir-Blodgett film of said organic material.



- 1 9. A sensor in accordance with claim 1, comprising  
means for compensating a background deflection of the flexible element  
(5).
- 5 10. A sensor in accordance with claim 9, wherein  
the compensating means comprises a pair of flexible elements (5, 51)  
made of identical materials, only one having the chemical sensing layer  
(23), means (8, 10) for determining the deflections of both flexible  
elements (5, 51) simultaneously, and further means (52) for determining  
the difference between said deflections.
- 10 11. An array, comprising at least two sensors in accordance with claim 1,  
wherein each sensor has a different chemical sensing layer (23).
12. An array, comprising at least two sensors in accordance with claim 4 ,  
wherein the chemical sensing layers (23) of said two sensors have  
different temperatures under operating conditions.

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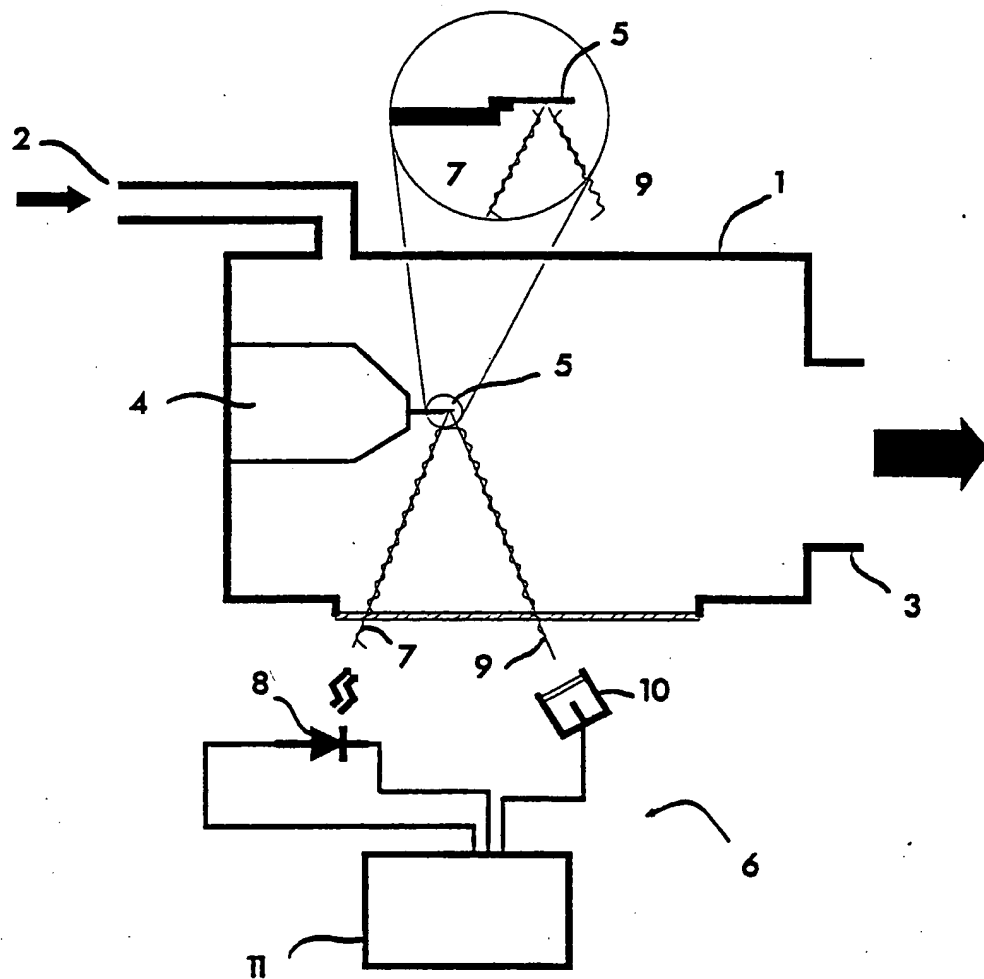


FIG.1

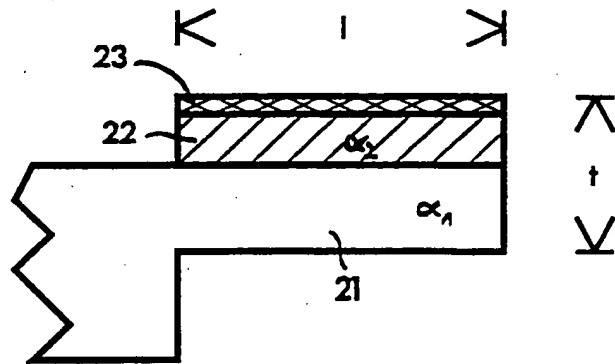


FIG. 2A

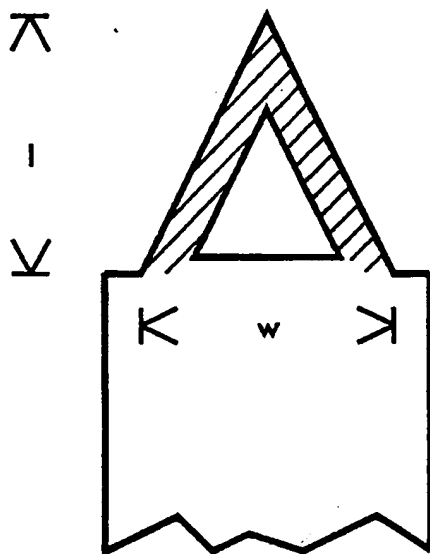


FIG. 2C

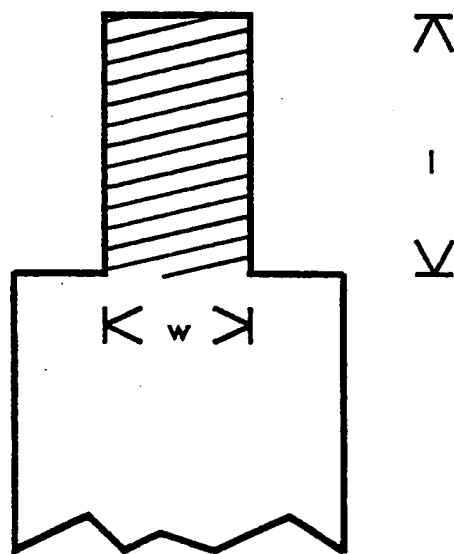


FIG. 2B

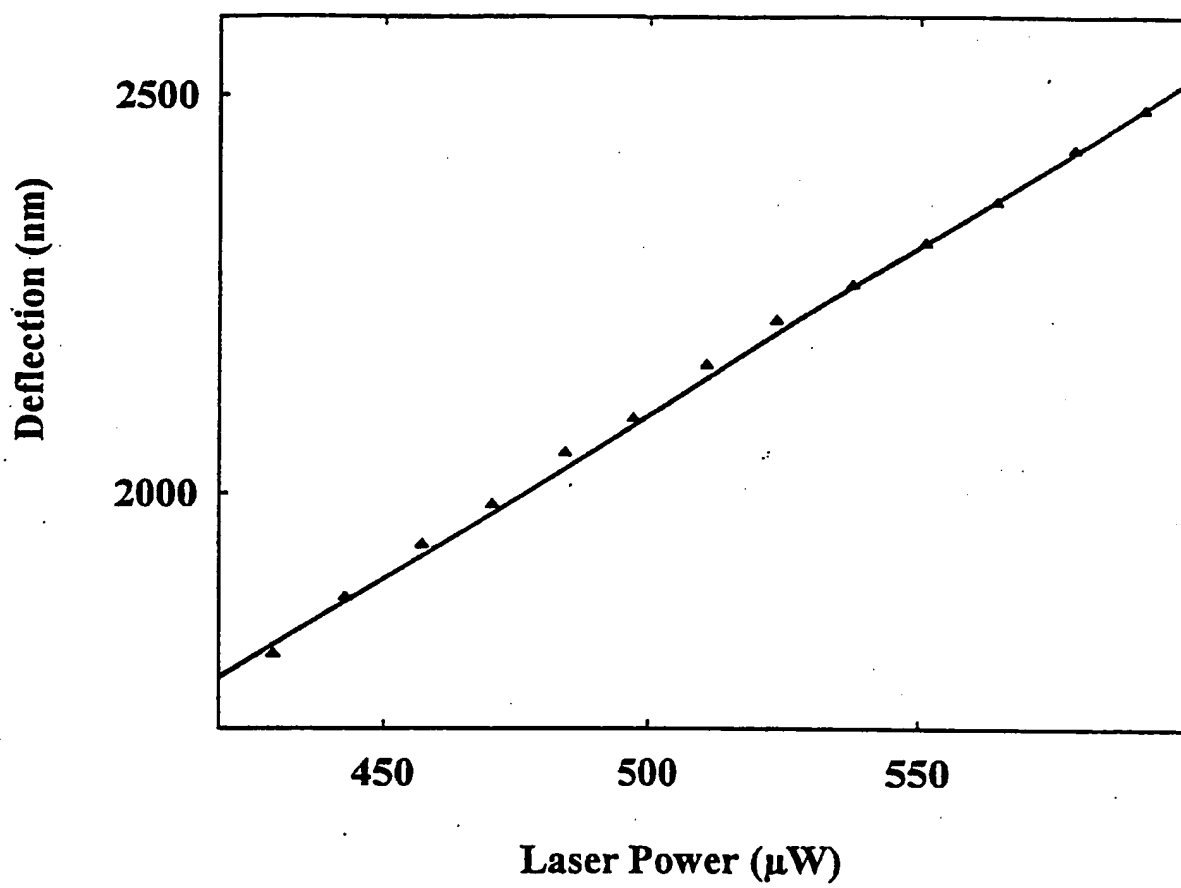


FIG.3

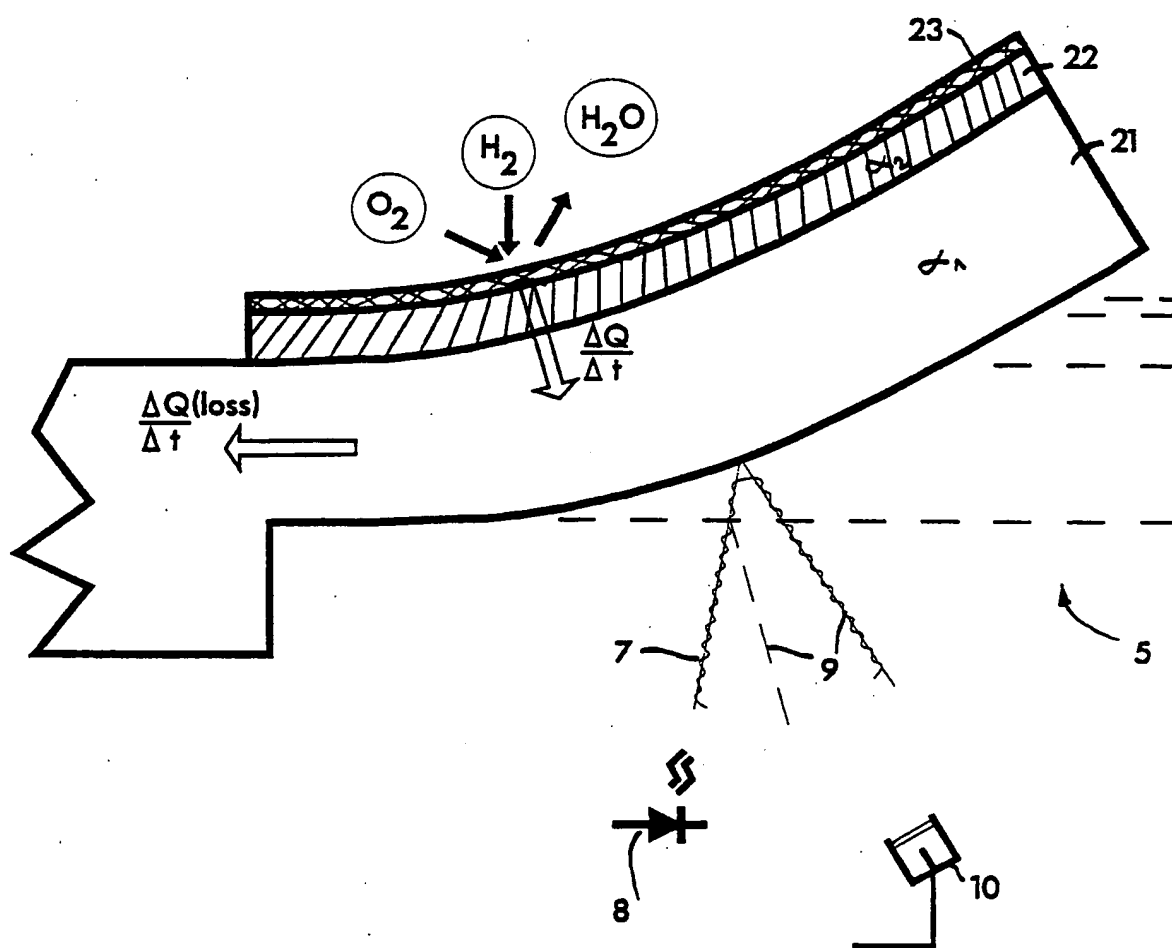


FIG.4

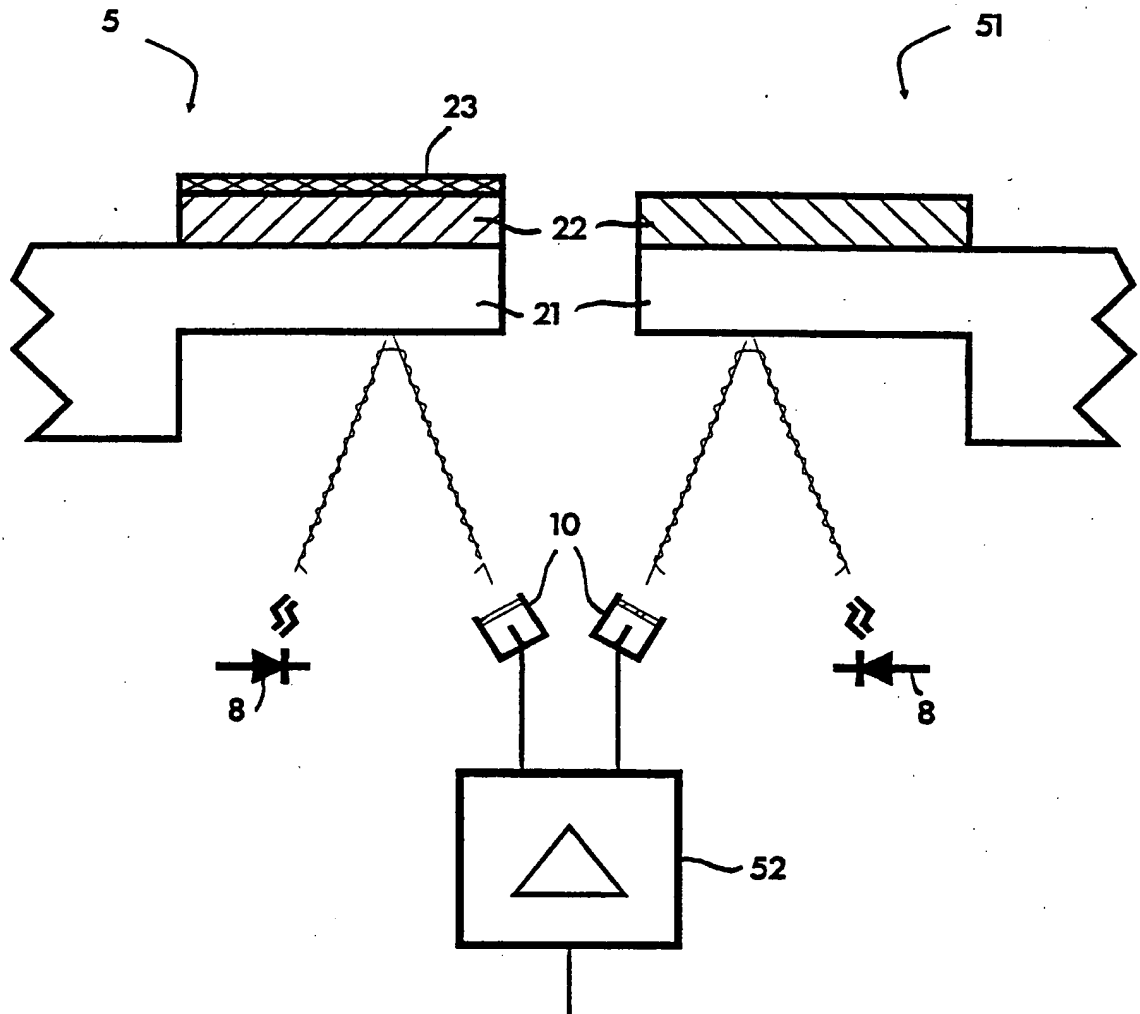


FIG.5

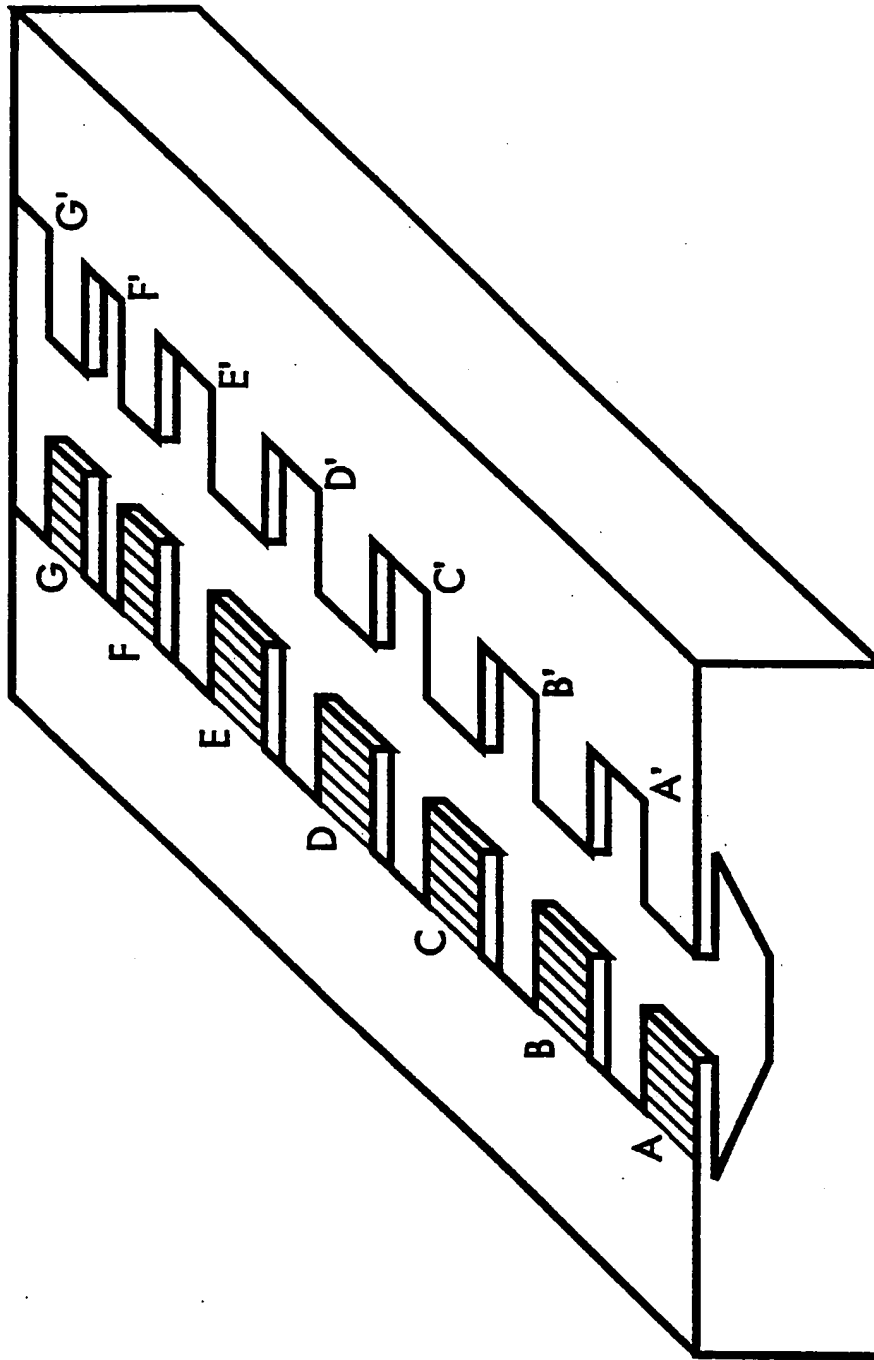


FIG.6

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01742

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G01N25/36 H01H1/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01B G01N H01H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,C,875 881 (CONCORDIA ELEKTRIZITÄTS-AKTIENGESELLSCHAFT) 8 July 1949 see the whole document ---	1-7,9,10
Y	WO,A,89 09477 (FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 5 October 1989 see the whole document ---	1-7,9,10
Y	US,A,2 745 721 (C.TIFFANY ; N.J.ENGLEWOOD) 15 May 1956 see especially column 3 ,lines 30-66, fig 1 see the whole document ---	1,2,4-7
Y	US,A,2 881 274 (W.A.RAY) 7 April 1959 see the whole document ---	1,2,4-7
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 March 1994

Date of mailing of the international search report

05.04.94

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Brock, T



# INTERNATIONAL SEARCH REPORT

Int ernational Application No

PCT/EP 93/01742

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	IEEE TRANSACTIONS ON ELECTRON DEVICES vol. ED25, no. 10 , October 1978 , NEW YORK US pages 1241 - 1250 K.E.PETERSEN 'dynamic micromechanics on silicon : techniques and devices' cited in the application ----	1-3,11, 12
A	FR,A,2 287 698 (DICTAPHONE CORP) 7 May 1976 cited in the application ----	1
A	EP,A,0 511 662 (MATSUSHITA ELECTRIC INDUSTRIAL CO LTD) 4 November 1992 see page 5, line 29 - page 13, line 39; claims 1,4-9; figures 1-9 -----	1,8

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

Int: ional Application No

PCT/EP 93/01742

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-C-875881		NONE	
WO-A-8909477	05-10-89	DE-A- 3809597	05-10-89
US-A-2745721		NONE	
US-A-2881274		NONE	
FR-A-2287698	07-05-76	US-A- 3959764	25-05-76
		DE-A, C 2543024	22-04-76
		GB-A- 1501888	22-02-78
		US-A- 4068021	10-01-78
EP-A-0511662	04-11-92	JP-A- 4330281	18-11-92
		JP-A- 5093623	16-04-93